A Critical Link between Amorphous Structure and Quasicrystal Formation

Significance

Medium range order (MRO) in amorphous structures is difficult to measure experimentally. This work demonstrated that Fluctuation Electron Microscopy (FEM) permits experimental access to MRO. The significance of this work is that it has provided a more detailed picture of amorphous structure at the regime of medium range order, elucidated the structural origin of phase transformation to the icosahedral phase, and opened an opportunity to establish structure-property relationships. The information obtained will be valuable for the use of amorphous materials as structural and functional materials and as precursor to nanostructured materials needed by nanotechnology through well controlled crystallization.

Scientific Achievement

It has been speculated widely that the degree of short- or medium-range order in amorphous Zr-based alloys plays an important role on crystallization behavior, with such order necessary to lead to crystallization of quasicrystalline phases. Fluctuation Electron Microscopy (FEM) is a direct probe of medium-range order and thus provides unique capability to probe amorphous structures. In this work, we have employed FEM to provide the first direct evidence of the role of medium-range order on the crystallization of amorphous Zr-based alloys.

The amorphous Zr-based alloys studied were prepared by one of two fundamentally different processes: rapid solidification (RS) or mechanical milling (MM). Conventional diffraction suggests the structures of these two materials are fully amorphous and indistinguishable. However, their crystallization behaviors as monitored by differential scanning calorimetry are distinct. While mechanically milled powders (MMP) crystallize directly into equilibrium phases, rapidly solidified ribbon (RSR) first crystallizes into the metastable icosahedral (quasicrystalline) phase. It has been proposed that rapid solidification leads to frozen-in local correlations which are predominantly icosahedral. The preexisting icosahedral local order lowers the nucleation barrier and thus promotes the icosahedral phase formation. Comparison of medium range order (MRO) measured by FEM showed a much higher degree of MRO in the amorphous phase prepared by RS as compared to that in the amorphous pahses prepared by MM. Furthermore, RS materials exhibited a large increase in MRO as a function of annealing. These are the first direct measurements that implicate the role of MRO on quasicrystal formation. Based on this data, we conclude that the preexisting MRO plays a critical role in crystallization and is the structural origin of the icosahedral phase.

Performers:

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Electron microscopy was carried out in the Electron Microscopy Center at Argonne National Laboratory

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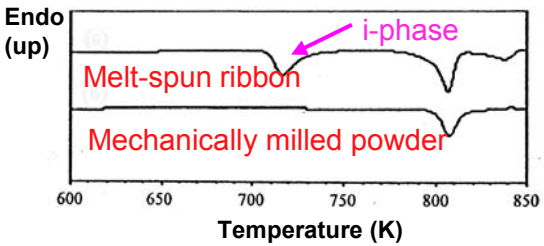
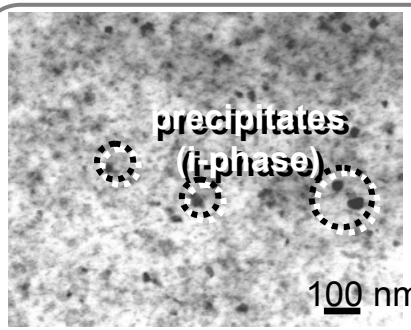
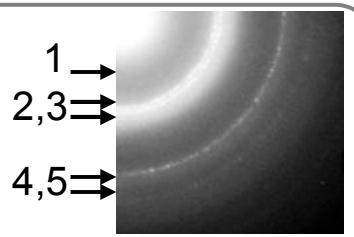
- **We have established the critical link between pre-existing medium range order (MRO) in the amorphous phase and icosahedral quasicrystal (IQC) formation in Zr-based alloys.**

Differential scanning calorimetry reveals formation of IQCs in MSR

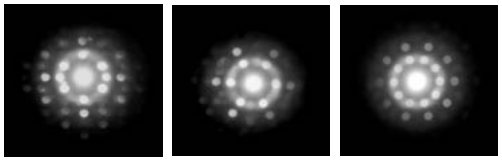


The structure of amorphous Zr-based alloys prepared in two ways appear indistinguishable by conventional diffraction, but crystallization behavior is very different.





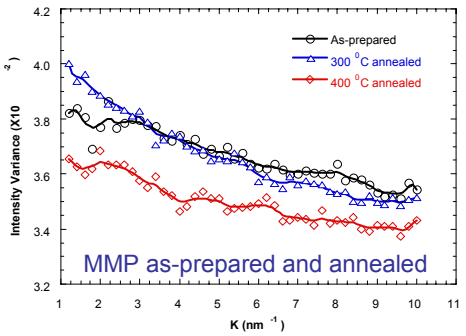
1 - (110001) 2 - (100000)
3 - (110000) 4 - (101010)
5 - (200000)

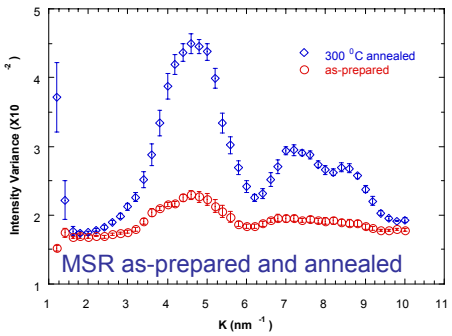


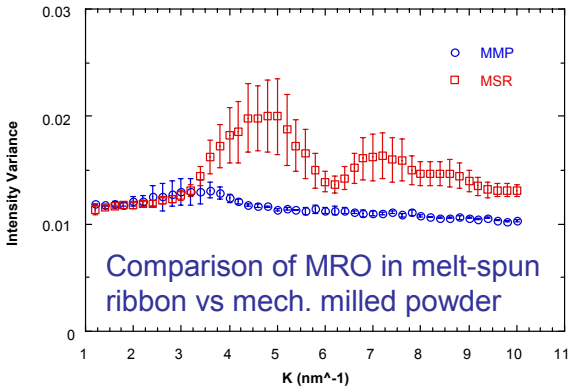
Precipitates with 2-fold, 3-fold and 5-fold symmetries

TEM confirms the formation of IQCs in melt-spun ribbon

- **Fluctuation electron microscopy, which provides unique information about order in amorphous materials, reveals remarkable differences in the degree of medium range order, providing the correlation between MRO and IQC formation.**







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